

PATENT SPECIFICATION

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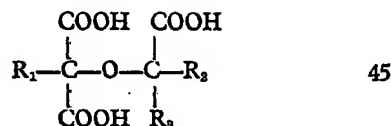
(54) NOVEL CARBOXYLIC ACIDS AND DERIVATIVES

(71) We, MONSANTO COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of 800 North Lindbergh Boulevard, St. Louis, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to novel polycarboxylic acids and derivatives including compounds which are useful as sequestrants detergency builders, and to detergent formulations containing such compounds. Numerous materials are known which, by virtue of sequestering characteristics and/or capability to enhance the cleansing ability of detergent formulations in combination with various surfactants are useful in water treating applications, or as adjuvants, re-enforcers, supplements, augmentors potentiators and/or benefactors in detergent formulations wherein such materials are usually referred to as detergency builders. It is noted that although many detergency builders are also sequestrants, the determination of materials which are effective detergency builders is a complex matter empirical in nature and not accurately predictable from known characteristics of the materials.

Many materials of the foregoing type are characterized by high phosphorus content such as the alkali metal tripolyphosphates widely employed as detergency builders. It has recently been suggested by some researchers that such compounds may contribute to the acceleration of eutrophication processes. Accordingly, particularly in the detergent builder field, extensive efforts have been exerted to provide alternative function compounds free of phosphorus.

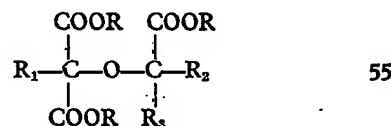
The novel compounds of the present invention are polycarboxylic acids having the formula



wherein each of R₁ and R₂ represents hydrogen or an alkyl group, and R₃ represents hydrogen, an alkyl group or a carboxyl group; their salts and their esters.

When any of R₁, R₂ and R₃ is an alkyl group, this is usually an alkyl group containing from 1 to 4 carbon atoms.

A preferred class of compounds is represented by the formula

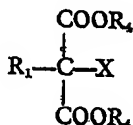


wherein each R is hydrogen, methyl, ethyl, alkali metal or ammonium; R₁ and R₂ are each hydrogen, methyl, or ethyl; and R₃ is hydrogen, methyl, ethyl or COOR.

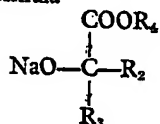
Thus the preferred compounds for use as detergency builders are the sodium salts and the ammonium salts. The new salts generally, however, include salts with any metal or any amine sufficiently basic to form a salt with a carboxylic acid.

Similarly, although the usual esters are the esters of alkanols having from 1 to 4 carbon atoms, specifically methanol and ethanol, the new compounds include partial and full esters of the polycarboxylic acids with any alcohol or phenol capable of entering into ester formation with a carboxylic acid.

The compounds (except those in which R₁ and R₂ are hydrogen and R₃ is COOR) can be prepared by reacting the appropriate halomalonate of the formula



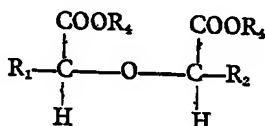
wherein R_4 is methyl or ethyl, R_1 is as defined in the formula above, and X is chlorine or bromine but is chlorine when R_1 is hydrogen, with a sodium salt of an α -hydroxy ester of the formula



wherein R_4 is methyl or ethyl and R_2 and R_3 are as defined above in an inert solvent such as 1,2-dimethoxyethane or tetrahydrofuran.

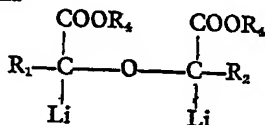
This reaction yields the ester forms of the compounds of this invention which can be saponified by conventional techniques to yield the desired ammonium or alkali metal salts, or hydrolyzed to the acids. Alternatively, the acid forms of the compounds of this invention can be obtained by acidifying the salts. The acids can be crystallized by conventional techniques to provide useful precursors for high purity salts. It is noted that when R_1 is hydrogen, the acid is relatively unstable due to a tendency to undergo rapid decarboxylation.

Those compounds in which R_3 is COOR , including those in which R_1 and R_2 are hydrogen can be prepared by adding a solution (preferably about 1 molar) of compounds represented by the formula

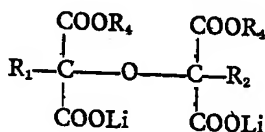


in tetrahydrofuran to two equivalents of lithium diisopropylamide or butyl lithium in tetrahydrofuran solution (preferably about 1 molar) at a temperature of about -78°C .

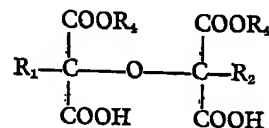
It is believed that this procedure results in formation of a lithium salt represented by the formula



Gaseous CO_2 is then introduced to form



The dilithium salt is converted to a half-ester half-acid



by treatment with an organic strong acid cation exchange resin, for example, a sulfonated polystyrene resin such as marketed by Fischer Scientific Co., under the trademark Rexyn 101(H). The full-ester forms can be obtained by conventional esterification procedures, and the full-acid forms by conventional hydrolysis. The salt forms are obtained by saponification of the half-ester half-acid.

In one preferred embodiment of the invention, R is sodium and R_1 , R_2 and R_3 are hydrogen. In another preferred embodiment, R is sodium, R_1 is methyl and R_2 and R_3 are hydrogen. In another preferred embodiment, R is sodium, R_1 and R_2 are hydrogen and R_3 is COONa . These embodiments are preferred by virtue of availability of raw materials for their manufacture and their excellent performance as detergency builders.

Both the acid and salt forms of the compounds of this invention are useful as metal ion sequestrants and as detergency builders, the use of the salt form being preferred.

The detergent formulations utilizing the compounds of this invention will contain from 1 to 75% by weight, preferably from 5 to 50% by weight of the salt, preferably sodium salt forms of the compounds of this invention. Such compounds can be utilized as the sole detergency builder in the compositions or in combination with other known detergency builders such as water soluble inorganic builder salts, for example, alkali metal carbonates, borates, phosphates, polyphosphates, bicarbonates and silicates or organic builders such as salts of phytic acid, sodium citrate and water soluble polymeric polycarboxylates as described in U.S. Patent 3,308,067.

The detergent formulations will additionally contain at least 8% by weight of a surfactant. Any of the numerous well known anionic, nonionic zwitterionic or ampholytic surfactants can be employed.

Examples of suitable anionic surfactants include alkyl ethyl sulfonates, alkyl sulfates, acyl sarcosinates, acyl esters of isocyanates, acyl N-methyl taurides, and alkyl aryl sulfonates. The foregoing materials are used in the form of their water-soluble sodium, potassium, ammonium and alkyl ammonium salts. Specific examples include sodium lauryl sulfate; sodium N-methyl lauryl tauride; sodium dodecyl benzene sulfonate; and triethanol amine undecanol benzene sulfonate.

Examples of suitable nonionic detergents include alkyl phenol and alcohol alkoxyates

including condensates of 1 - decanol or 1 - undecanol with from 3 to 5 molecular proportions of ethylene oxide; condensates of monohydroxy or polyhydroxy alcohols such as oleyl alcohol or 1 - tridecanol with from 9 to 15 molecular proportions of ethylene oxides; alkyl internal vicinal dialkoxy or hydroxy alkoxy compounds as described in Belgian Patent No. 782,369; and condensates of alkylene oxides with organo amines, for example, ethylene diamine and amides such as N - octadecyl diethanol amide.

Suitable ampholytic surfactants include the amido alkene sulfonates such as sodium C-pentadecyl, N - methyl amido ethyl sulfonate; potassium C - octyl N - naphthalene amido propyl sulfonate; ammonium C - decyl, N - cyclo propyl amido butyl sulfonate; and aliphatic amine derivatives in which the aliphatic substituent contains an anionic water-solubilizing substituent such as a carboxy, sulfo, phosphato, or phosphino group, for example, sodium - 3 - dodecyl amino propionate and sodium - 3 - dodecyl amino propane sulfonate.

Examples of zwitterionic surfactants include derivatives of quaternary ammonium phosphonium and sulfonium compounds such as 3 - (N,N - dimethyl - N - hexadecyl ammonio) propane - 1 - sulfonate and 3 - (N,N - dimethyl - N - hexadecyl ammonio - 2 - hydroxy propane - 1 - sulfonate).

It will be understood that the above examples of supplementary surfactants are by no means comprehensive. Numerous other surfactants are known to those skilled in the art and are set forth in such familiar references as Surface Active Agents by A. M. Schwarz and James W. Perry. It will be further understood that the use of such surfactants will be in accordance with conventional, well-understood practice of detergent formulation. For example, cationic and anionic detergents will not normally be employed in combination due to recognized problems of precipitation of insoluble products.

In accordance with general practice, the ratio of the detergency building components to the surfactant components will be in the range of from 1:2 to about 12:1 by weight.

In addition to surfactant and builder components, the detergent formulations may contain fillers such as sodium sulfate and minor amounts of bleaches, dyes, optical brighteners, soil anti-redeposition agents, perfumes and similar conventional detergent formulation additives.

It is further expected that the compounds of this invention will function effectively in machine dishwashing formulations as total or partial replacements for sodium tripolyphosphate.

The invention is further illustrated by the following Examples wherein all parts and

percentages are by weight unless otherwise indicated.

EXAMPLE I

To a slurry of 34 grams sodium ethyl glycolate in 300 ml of 1,2 - dimethoxyethane is added with stirring a solution of 63 grams diethyl 2 - bromo - 2 - methylmalonate in 100 ml of 1,2 - dimethoxyethane precooled to 5°C. During slurry addition, the temperature is maintained below 10°C. The reaction mixture is maintained at 25°C for 16 hours and at 65°C for 2 hours with stirring. Solids are recovered by filtration and solvent removed under reduced pressure. The residue is dissolved in CHCl_3 and the solution is washed, in succession, with .5 normal HCl, saturated Na_2CO_3 , and water. The solution is then dried over anhydrous MgSO_4 and the CHCl_3 removed under reduced pressure. The residue is fractionally distilled with product being collected at 95—97°C, 0.04 mm Hg.

The product is identified as triethyl 2 - oxa - 1,3,3 - butane tricarboxylate by nuclear magnetic resonance and elemental analysis.

The ester is saponified in an aqueous ethanol solution of sodium hydroxide at room temperature. Acidifying the solution with H_2SO_4 yields the acid which is extracted with ether and crystallized therefrom.

Pouring the saponified solution into excess methanol precipitates the salt.

EXAMPLE II

The salt and acid produced according to Example I are tested for sequestration characteristics and are found to effectively sequester Ca^{++} ions.

EXAMPLE III

Detergent formulations containing 12% linear alkyl - benzene sulfonate having an average alkyl chain length of about 12 carbon atoms; from 5 to 75% trisodium 2 - oxa - 1,3,3 - butanetricarboxylate; 12% sodium silicate having an SiO_2 to Na_2O ratio of about 2.4; and a quantity of sodium sulfate sufficient to equal 100% are found in conventional laundry operations, to clean soiled samples of cotton and polyester cotton broadcloth substantially better than otherwise identical formulations containing no trisodium 2 - oxa - 1,3,3 - butanetricarboxylate. These tests demonstrate that this material is an effective detergency builder material.

EXAMPLE IV

The tests of Example III above are repeated using a detergent formulation in which Neodol 45-11 (a nonionic surfactant which is an adduct of a modified oxo type C_{14} — C_{15} alcohol with an average of 11 moles of ethylene oxide) is substituted for the alkylbenzene sulfonate. Comparable results are obtained.

EXAMPLE V

The tests of Example III are repeated with a detergent formulation wherein sodium hydroxyalkyl (C_{14} — C_{16} alkyl chain length) N - methyl laurate, an ampholytic surfactant, is substituted for the alkylbenzene sulfonate. Comparable results are obtained.

EXAMPLE VI

The tests of Example III are repeated with a detergent formulation wherein cocodimethylsulfopropylbetaine (where "Coco" indicates a mixture of fatty acid radicals derived from coconut fatty acid), a zwitterionic surfactant is substituted for the alkylbenzene sulfonate. Comparable results are obtained.

EXAMPLE VII

To a slurry of 72 grams of sodium ethyl glycolate in 350 ml of 1,2 - dimethoxyethane at 50—65°C is added 97 grams of diethyl chloromalonate over a two hour period. The resulting solution is refluxed until a neutral pH is obtained. The reaction mix is then stirred for 16 hours at 25°C and reaction product isolated as in Example I, the product being collected at 119—120°C, 0.5 mm Hg. The product is identified as triethyl 2 - oxa - 1,1,3 - propane - tricarboxylate. Salts and acid forms of the product are prepared as in Example I and are found to be effective sequestrants for Ca^{++} ions.

EXAMPLE VIII

Detergent formulations containing from 5%—75% trisodium 2 - oxa - 1,1,3 - propanetricarboxylate are prepared and tested as in Examples III—VI. Comparable results are obtained.

EXAMPLE IX

A solution of 63 grams diethyl 2 - bromo - 2 - ethylmalonate in 25 ml tetrahydrofuran is added to a slurry of 59 grams sodium diethylmethyltartronate in 300 ml tetrahydrofuran at 65°C. The mixture is refluxed for 18 hours after which the tetrahydrofuran is removed under vacuum and the residue diluted with ethyl ether. The ethereal solution is washed with water to remove NaBr, dried over anhydrous $CaSO_4$ and distilled to remove the ether.

The residue is fractionally distilled, product being collected at 130—135°C (0.06 mm Hg). The product is identified as tetraethyl 3 - oxa - 2,2,4,4 - hexanetetracarboxylate by nuclear magnetic resonance and elemental analysis.

The sodium salt is obtained by saponification in a methanol solution of sodium hydroxide at room temperature and recovered by filtration.

EXAMPLE X

To a slurry of 34 grams sodium ethyl glycolate in 300 ml tetrahydrofuran cooled to about 3°C is added a solution of 63 grams

diethyl 2 - bromo - 2 - ethylmalonate in 25 ml tetrahydrofuran at about 3°C. The mixture is maintained at 0°—5°C with stirring for 2 hours, warmed to and maintained at about 25°C for 16 hours and then refluxed for 2 hours.

The tetrahydrofuran is removed under vacuum and the residue treated as in Example IX, the ester product triethyl - 2 - oxa - 1,3,3 - pentanetricarboxylate being collected at 101°C—107°C (0.05 mm Hg) and converted to the salt form as described in Example IX.

EXAMPLE XI

Sodium ethyl lactate (38 grams) and diethyl 2 - bromo - 2 - ethylmalonate are reacted according to the procedure of Example X to yield an ester product triethyl - 3 - oxa - 2,4,4 - hexanetricarboxylate being collected at 92°C—96°C (0.04 mm Hg) which is converted to the salt form as described in Example X.

EXAMPLE XII

To a slurry of 98 grams of sodium ethyl lactate in 400 ml 1,3 - dimethoxyethane at room temperature is added 136 grams diethyl chloromalonate. The mixture is heated at 70°C for 8 hours and then maintained at 25°C for 48 hours. The 1,2 - dimethoxyethane is evaporated and the residue dissolved in carbon tetrachloride, washed with water to remove NaCl, dried over $MgSO_4$ and the $CHCl_3$ evaporated. Fractional distillation of the residue gives a product (b.p. 94°C—96°C @ 0.03 mm Hg) analytically identified as triethyl 2 - oxa - 1,1,3 - butanetricarboxylate. Saponification of the ester with NaOH yields trisodium 2 - oxa - 1,1,3 - butanetricarboxylate.

EXAMPLE XIII

To a slurry of 77 grams of sodium ethyl lactate in 300 ml 1,2 - dimethoxyethane at 45°C is added a solution of 127 grams diethyl 2 - bromo - 2 - methylmalonate in 1,2 - dimethoxyethane and the temperature is allowed to rise to about 65°C. The mixture is refluxed until the pH of an aqueous solution of the mixture is about 7. The 1,2 - dimethoxyethane is evaporated, the residue washed with water to remove NaBr. Distillation of the dried residue yields a product (collected at 82°C, 0.05 mm Hg) analytically identified as triethyl 3 - oxa - 2,2,4 - pentanetricarboxylate. Saponification of the ester with NaOH yields trisodium 3 - oxa - 2,2,4 - pentanetricarboxylate.

EXAMPLE XIV

A 1 liter flask is purged with nitrogen, charged with 400 ml tetrahydrofuran and cooled to —30°C in a dry-ice acetone bath. 115 ml 2.3 molar solution of n - butyllithium

in tetrahydrofuran is added and the solution cooled to -75°C . A solution of 21 grams diethyl diglycolate in 100 ml tetrahydrofuran is added, the temperature being maintained below 70°C . CO_2 is then bubbled into the mixture for about an hour and the mixture warmed to room temperature, the tetrahydrofuran is evaporated leaving a yellow powder. The powder is dissolved in water and 100 ml of Rexynl 101(H) ion exchange resin added. An insoluble gum separates and is removed. The remaining solution is then passed through a column packed with sufficient resin to complete the conversion to the half-ester half-acid.

The water solution of half-acid half-ester product is dried to a syrup. This material is dissolved in 25 ml ethanol, 40 ml benzene and 0.2 grams concentrated H_2SO_4 . Water is azeotropically removed and the residue diluted with benzene, washed with NaHCO_3 solution and then water and dried over MgSO_4 . The benzene is evaporated and the residue distilled. Product collected at 141°C — 142°C (0.05—1 mm Hg) is identified as tetraethyl 2 - oxa - 1,1,3,3 - propanetetracarboxylate.

Alternatively, saponification of the half-acid half-ester with sodium hydroxide yields tetraethyl 2 - oxa - 1,1,3,3 - propanetetracarboxylate.

EXAMPLE XV

To a slurry of 56 grams sodium diethyl methyltartronate in 300 ml of refluxing tetrahydrofuran is added a solution of 63 grams diethyl - 2 - bromo - 2 - methylmalonate in 25 ml tetrahydrofuran and the mixture refluxed for about 16 hours. The solvent is evaporated and the residue diluted with ethyl ether. NaBr is removed by washing the ethereal solution with water and the washed solution is dried over CaSO_4 and MgSO_4 and solvent evaporated.

Distillation of the residue yields a fraction collected at 125°C (0.05 mm Hg) identifiable as tetraethyl - 3 - oxa - 2,2,4,4 - pentanetetracarboxylate.

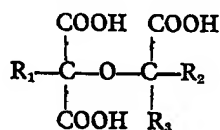
Saponification with NaOH yields the tetrasodium salt.

EXAMPLE XVI

Detergent formulations containing 5%—75% of the salt forms of the compounds produced according to Examples IX—XV are prepared and tested as in Examples III—VI. Comparable results are obtained.

WHAT WE CLAIM IS:—

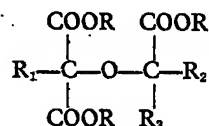
1. A polycarboxylic acid having the formula



wherein each of R_1 and R_2 represents hydrogen or an alkyl group, and R_3 represents hydrogen, an alkyl group or a carboxyl group; or a salt or ester of such an acid.

2. A polycarboxylic acid, ester or salt according to Claim 1 wherein each of R_1 and R_2 represents hydrogen or an alkyl group of from 1 to 4 carbon atoms, and R_3 represents hydrogen, an alkyl group of from 1 to 4 carbon atoms or a carboxyl group.

3. A compound having the formula



wherein each R is hydrogen, methyl, ethyl, alkali metal or ammonium; R_1 and R_2 are each hydrogen, methyl, or ethyl; and R_3 is hydrogen, methyl, ethyl or COOR .

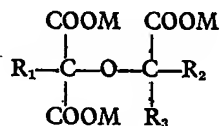
4. A compound according to Claim 3 wherein R is sodium.

5. A compound according to either of Claims 3 and 4 wherein R_1 , R_2 and R_3 are each hydrogen or methyl.

6. A compound according to Claim 5 wherein R_1 and R_2 are hydrogen or methyl and R_3 is hydrogen.

7. A compound according to either of Claims 3 and 4 wherein R_3 is COOR and R_1 and R_2 are hydrogen or methyl.

8. A detergent composition comprising at least 8% by weight of a surfactant selected from anionic, nonionic, zwitterionic and ampholytic surfactants, and from 1% to 75% by weight of a detergency builder compound having the formula



wherein each M is alkali metal or ammonium, R_1 and R_2 are each hydrogen, methyl or ethyl, and R_3 is hydrogen, methyl, ethyl or COOM .

9. A composition according to Claim 8 in which the detergency builder compound constitutes from 5% to 50% of the weight of the composition.

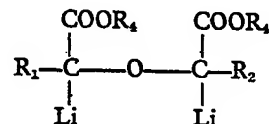
10. A composition according to either of Claims 8 and 9 wherein M is sodium.

11. A composition according to any of Claims 8, 9 and 10 wherein R_1 , R_2 and R_3 in the detergency builder compound are each hydrogen or methyl.

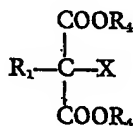
12. A composition according to Claim 11 wherein R_1 and R_2 are hydrogen or methyl substituents and R_3 is hydrogen.

13. A composition according to Claim 12 wherein each of R_1 , R_2 and R_3 is hydrogen.

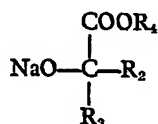
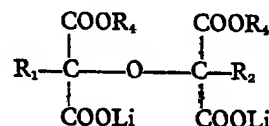
14. A composition according to any of Claims 8, 9 and 10 wherein R_3 is COOM and R_1 and R_2 are methyl. 35
- 5 15. A composition according to any of Claims 8, 9 and 10 wherein R_3 is COOM, R_1 is methyl and R_2 is hydrogen.
16. Any compound according to Claim 3 that is described in either of Examples I and VII. 40
- 10 17. Any compound according to Claim 3 that is described in any of Examples IX to XV.
18. A composition according to Claim 8 substantially as described in any of Examples 15 III to VI and VIII.
19. A composition according to Claim 8 substantially as described in Example XVI.
- 20 20. A process for the production of a compound of Claim 3 (except one in which R_1 and R_2 are hydrogen and R_3 is COOR), which comprises reacting a halomalonate of the formula 45



wherein R_1 and R_2 are as defined in Claim 3 and R_4 is methyl or ethyl with carbon dioxide to give a compound 50



- 25 wherein R_4 is methyl or ethyl, R_1 is as defined in Claim 3, and X is chlorine or bromine but is chlorine when R_1 is hydrogen, with a sodium salt of an α - hydroxy ester of the formula



- 30 is an inert solvent to give an ester, which is then optionally hydrolysed to the acid or saponified to give an alkali metal or ammonium salt.

21. A process according to Claim 20 sub-

which is then converted to a half-ester, half-acid by treatment with an organic strong acid cation exchange resin, and the half-ester, half-acid is then optionally esterified to a full ester, hydrolysed to the full acid or saponified to a salt. 55

25. A process according to Claim 24 substantially as described in Example XIV.

26. A compound according to Claim 3 that has been obtained by a process according to either of Claims 24 and 25. 60

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